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(54) Title: STABILIZER COMPOSITIONS COMPRISING A MONOMERIC DIHYDROPYRIDINE DERIVATIVE AND THEIR
USE

(57) Abstract: The present invention pertains to a stabilizer composition for polymers comprising 1.5 - 23 % w/w of at least one polyol, 1.5 - 46 % w/w of at least one acid scavenger, 3.0 - 31 % w/w of at least one monomeric dihydropyridine derivative selected from the group of substituted or unsubstituted dihydropyridine dicarboxylic acid esters, ester amides, and diamides, 0 - 5 % w/w of one or more oxidizing agents, and 0 - 94 % w/w of one or more additives, based on the total weight of the stabilizer composition, and wherein the stabilizer composition does not comprise any beta-diketone. The present invention finally pertains to a stabilized polymer composition containing this stabilizer composition, to a process for preparing the same, to the use thereof for the production of moulded articles, and to the resulting moulded articles.

STABILIZER COMPOSITIONS COMPRISING A MONOMERIC DIHYDRO-
PYRIDINE DERIVATIVE AND THEIR USE

5

The present invention relates to novel stabilizer compositions for polymers and the use thereof for the stabilization of polymers. The present invention further pertains to a stabilized polymer so obtained, to a process for preparing the stabilized polymer, the use thereof for the production of
10 moulded articles, as well as the resulting moulded articles.

Organic polymers decompose to a greater or lesser extent at higher temperatures, e.g., during the manufacture of polymer articles and/or under the influence of oxygen, light, and moisture. This decomposition not only
15 results in an unwanted discoloration, but also in a reduction of the mechanical properties, leading, e.g., to a reduction of the residual stability in the plastic article produced, which in turn influences the durability of the article. In order to protect the resin and the articles produced from this resin against this decomposition, stabilizers are incorporated into or mixed with
20 the organic polymers.

A recent trend is the use of renewable stabilizer components, i.e. components that can be produced by natural processes, such as natural polyols and derivatives, to reduce the impact on the environment and the
25 amount of exhaustible raw materials used. However, though quite good thermal stabilization can be achieved with natural polyols, the colour stability of a polymer article, particularly a polyvinyl chloride article, containing natural polyols is low. It is therefore an object of the present invention to provide stabilizer compositions which comprise a renewable
30 stabilizer component and which, at the same time, show a good thermal stability and a good colour stability.

A stabilizer composition comprising renewable stabilizer components is disclosed, e.g., in EP-A-0 716 123. In the example of this reference a stabilizer composition for polyvinyl chloride is disclosed comprising a polydihydropyridine, a hydrotalcite, and a natural polyol. However, the heat and colour stability of the thus stabilized polyvinyl chloride is insufficient.

Further stabilizer compositions are disclosed, int. al., in EP-A-0 362 012, EP-A-0 049 699, and EP-A-0 005 678.

10 EP-A-0 362 012 discloses a stabilizer composition which comprises at least one beta-diketone, at least one hydrotalcite, and at least one dihydropyridine. A polyol is mentioned as further optional stabilizer component. The price-performance ratio of the stabilization compositions as disclosed herein is insufficient. There is no suggestion that (renewable) polyols, or derivatives thereof, can be used instead of the more expensive beta-diketone.

EP-A-0 049 699 mentions a combination of a beta-aminocrotonate and a dihydropyridine as heat stabilizer for polyvinyl chloride. However, most beta-aminocrotonates have the disadvantage that ammonia is released at higher temperatures.

Numerous references also disclose stabilizer compositions comprising large amounts of heavy metal-containing stabilizers, such as cadmium and/or lead compounds. However, these heavy metals are considered to pose a risk to health and the environment.

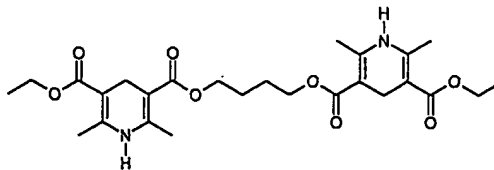
Furthermore, many of the prior art stabilizers are known to bloom from the stabilized polymer, which is undesired.

Accordingly, there is a need for alternative cost-efficient stabilizer compositions which comprise a polyol, preferably a renewable polyol, and/or derivatives of said (renewable) polyol, which compositions preferably do not release ammonia at higher temperatures, preferably do
5 not lead to blooming, which preferably are heavy metal-free, and which provide good heat and colour stability when used to stabilize a polymer.

It has now been found that most or all of these goals can be reached by using a stabilizer composition which is essentially free of a beta-diketone
10 and which comprises 1.5 - 23 per cent by weight (%w/w) of at least one polyol, 1.5 - 46 %w/w of at least one acid scavenger, 3.0 - 31 %w/w of at least one monomeric dihydropyridine derivative selected from the group of substituted or unsubstituted dihydropyridine dicarboxylic acid esters, ester
amides, and diamides, 0-5 %w/w of one or more oxidizing agents, and 0-94
15 %w/w of one or more additives, all weight percentages being based on the total weight of the stabilizer composition.

The polyol-containing stabilizer composition of the present invention leads to good heat as well as good colour stability. As is shown in the examples
20 below, the stabilizer composition of the present invention in particular has a better stabilizing effect than the stabilizer composition of EP-A-0 716 123, which contains a polydihydropyridine derivative instead of the monomeric dihydropyridine derivative of the present invention. In this context, it is noted that "monomeric" means that the dihydropyridine derivative of the
25 present invention contains only one dihydropyridine moiety. However, if so desired, the monomeric dihydropyridine derivative can be used in

combination with polymeric dihydropyridine derivatives, particularly dimeric



compounds, such as

The present invention relates to stabilizer compositions for polymers which
 5 are essentially free of a beta-diketone and comprise 1.5 - 23 %w/w of at
 least one (preferably renewable) polyol or derivative thereof, 1.5 - 46 %w/w
 of at least one acid scavenger, and 3.0 - 31 %w/w of at least one
 monomeric dihydropyridine derivative selected from the group of
 substituted or unsubstituted dihydropyridine dicarboxylic acid esters, ester
 10 amides and diamides, optionally 0-5 %w/w of one or more oxidizing agents,
 and 0 - 94 %w/w of one or more additives, all based on the total weight of
 the stabilizer composition.

The (preferably renewable) polyol or derivative thereof, hereinafter referred
 15 to as "polyol", as used in the stabilizer compositions of the present
 invention is preferably selected from the group consisting of pentaerithritol,
 dipentaerithritol, tripentaerythritol, bistrimethylol-propane, bistrimethylol-
 ethane, trimethylol-propane, trimethylol-ethane, tris-(hydroxyethyl)-
 isocyanurate (THEIC), tetramethylol cyclohexanol, tetramethylol
 20 cyclopentanol, tetramethylol cyclopyranol, carbohydrates such as sugars,
 sugar alcohols, the dehydration products of sugar alcohols, non-reducing
 oligo- and polysaccharides, and di-, oligo-, and polysaccharides the
 reducing unit of which has been reduced, cyclic polyalcohols and polymeric
 polyols, such as polyvinyl alcohol and copolymers thereof.

Suitable sugars are, e.g., glucose, galactose, fructose, iso(maltulose), leucrose, lactose, sucrose, glucose oligomers, such as maltose, isomaltose, cellobiose, maltotriose, (cyclo)dextrins, fructose oligomers, and mixed oligomers and mixtures of these sugars, as well as glycosides of
5 reducing sugars. Suitable sugar alcohols are, e.g., xylitol, arabinitol, sorbitol, mannitol, galactitol, lactitol, maltitol, (iso)maltitol, and maltotriol, with sorbitol being preferred. Suitable dehydration products of sugar alcohols are, e.g., sorbitan, galactitan, and mannitan. Suitable cyclic polyalcohols are, e.g., polyfructoses such as inulin and levan. Suitable
10 polysaccharides are, e.g., cellulose or starch. Preferably, the polyol comprises and more preferably consists essentially of a naturally occurring polyol.

An acid scavenger in the sense of the present invention is any compound
15 which, when present in a polymer, can de-activate the acidic substances present in said polymers. Such acidic substances are, e.g., acidic residues of Ziegler Natta catalysts in polyethylene, or any acidic compounds which can be formed during the processing of halogen-containing polymers, such as PVC.

20 The acid scavenger can be selected from the group of (a) natural and/or basic (mixed) metal compounds derived from inorganic and organic acids, such as substituted or unsubstituted, aliphatic or aromatic acids and phenols, (b) metal oxides and/or hydroxides, (c) layered ionic materials such as clays, (d) organic acid scavenging compounds, (e) silicates and/or
25 (f) (bi)carbonates, such as chalk. Preferred acid scavengers are selected from the compounds of groups (a)-(e), compounds of the groups (a)-(d) being most preferred.

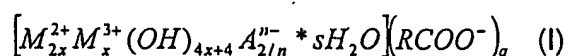
Suitable (mixed) metal compounds are, e.g., calcium hydrogen phosphite, calcium carbonate, calcium stearate, calcium p-tert-butylbenzoate, calcium benzoate-lactate, calcium lactate-stearate, calcium p-octylphenolate, calcium aluminium hydroxyphosphite, and similar compounds wherein
 5 magnesium is substituted for the calcium.

Suitable metal oxides and/or hydroxides are, e.g., calcium hydroxide, calcium oxide, similar compounds wherein magnesium is substituted for the calcium, and aluminium hydroxide. Suitable ionic layered materials are, e.g., magnesium-aluminium hydrotalcites, zeolites, and dawsonites. Finally,
 10 suitable organic compounds are, e.g., dicyandiamides, amines, melamines or urea derivatives.

Preferably, the acid scavenger is selected from one or more compounds of the group of natural and/or basic (mixed) metal compounds as described
 15 above, and layered ionic clays. More preferably, the acid scavenger comprises and most preferably consists essentially of a layered ionic clay, which preferably is a hydrotalcite.

The hydrotalcite preferably satisfies formula (I)

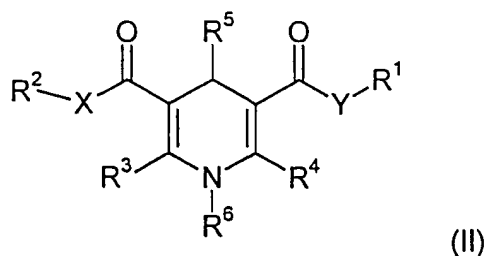
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M^{2+} represents one or more divalent metal cations selected from, e.g., zinc, calcium, iron and/or magnesium, with magnesium being most preferred.
 25 M^{3+} stands for one or more trivalent metal cations selected from, e.g., aluminium, iron, cobalt and/or chromium, with aluminium being most preferred. A^{n-} represents one or more n valent anions, such as hydroxide, chloride, bromide, iodide, perchlorate, sulphate, bicarbonate, carbonate,

oxalate, hexacyanoferrate and/or monocarboxylic acid moieties RCOO^- with, e.g., 2 - 22 carbon atoms, wherein R represents a cyclic, branched or linear, saturated or non-saturated alkyl or aryl group. A typical carboxylate is acetate. Index x is a positive number preferably satisfying $1.5 < x < 5$, n, s, and q preferably satisfy $1 < n < 4$, $0 < s < 4$, and $0 \leq q < 4$, respectively.

As stated above, the monomeric dihydropyridine derivative is selected from the group of substituted or unsubstituted dihydropyridine dicarboxylic acid esters, dihydropyridine ester amides, and dihydropyridine diamides. Substituted dihydropyridine moieties may carry substituents either on the dihydropyridine ring and/or, in the case of ester amides or amides, on the amide groups. The monomeric dihydropyridine dicarboxylic acid esters, ester amides, and diamides can generally be described by the following formula (II)

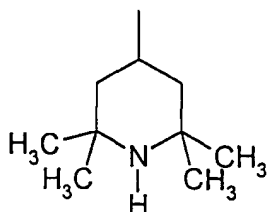


In formula (II) X and Y may be independently chosen from O or NR, representing the dihydropyridine dicarboxylic acid esters, amides, and ester amides, respectively, with R being selected from the group of substituted or unsubstituted alkyl, alkenyl, cycloalkyl, optionally containing heteroatom(s), such as O, S or N, in the ring, aryl, alkaryl or arylalkyl groups having up to 20 carbon atoms, or hydrogen.

R^1 and R^2 are independently selected from the group of substituted or unsubstituted alkyl, alkenyl, cycloalkyl, optionally containing heteroatom(s), such as O, S or N, in the ring, aryl, alkaryl or arylalkyl groups having up to 20 carbon atoms, or hydrogen in the case of X and/or Y being NR.

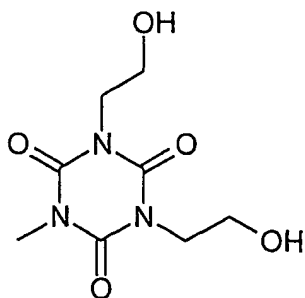
- 5 R^3 , R^4 , R^5 , and R^6 are independently selected from hydrogen or substituted or unsubstituted alkyl, alkenyl, cycloalkyl, aryl, alkaryl or arylalkyl groups having up to 22 carbon atoms.

Suitable substituents for the alkyl, alkenyl, cycloalkyl, aryl, alkaryl or arylalkyl groups of R^1 and R^2 are, e.g., hydroxy, ether, thioether, ester, 10 halogen or (meth)acryloyloxy groups. Examples of preferred groups for R^1 and/or R^2 are ethyl, tert. butyl, undecyl, 2-ethylhexyl, propenyl, hydroxyethyl, methoxyethyl, 2-phenoxyethyl, benzyl, and a benzoic acid ethyl ester group. Examples of preferred cycloalkyl groups containing 15 heteroatom(s) in the ring are a hindered amine satisfying formula (IV)



(III)

and a cyanuric acid group satisfying formula (IV)

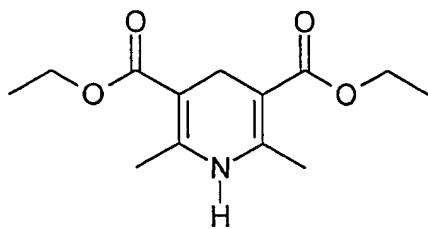


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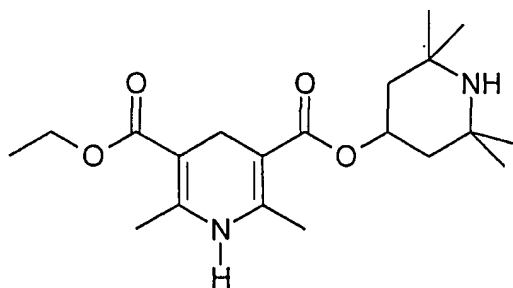
Most preferably, R^1 and R^2 independently are ethyl and/or benzyl groups.

Suitable substituents for the alkyl, alkenyl, cycloalkyl, aryl, alkaryl or arylalkyl groups of R^3 , R^4 , R^5 , and R^6 are, e.g., hydroxy and/or nitro groups. R^3 and R^4 preferably are not both H and still more preferably are both methyl. R^5 preferably is selected from hydrogen, alkyl, aryl or alkaryl groups and R^6 in formula (II) preferably is selected from hydrogen, benzyl or hydroxyethyl.

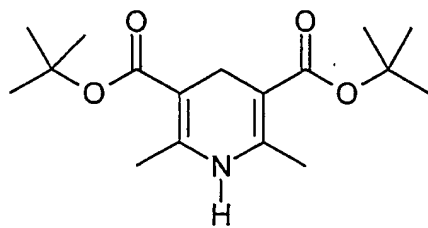
Examples of preferred dihydropyridine dicarboxylic acid esters are



(V)

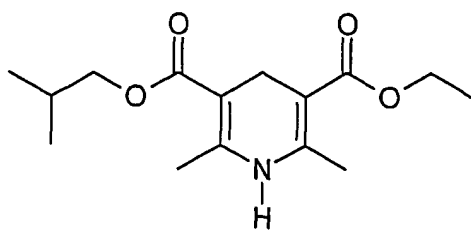


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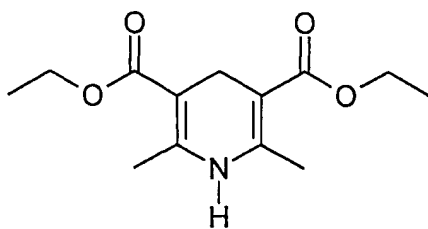


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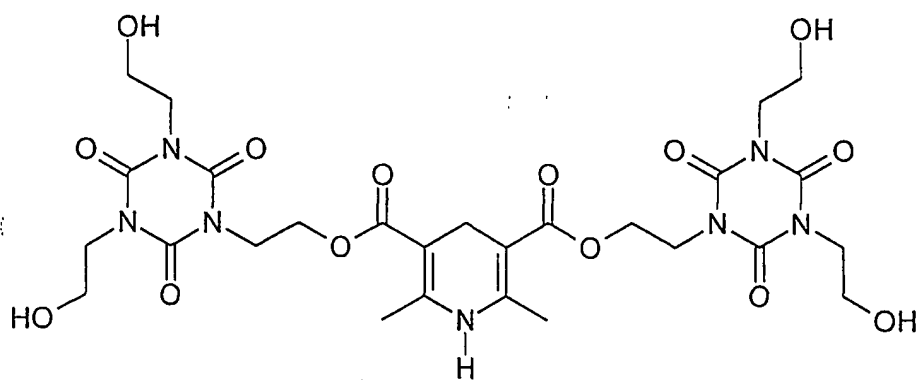
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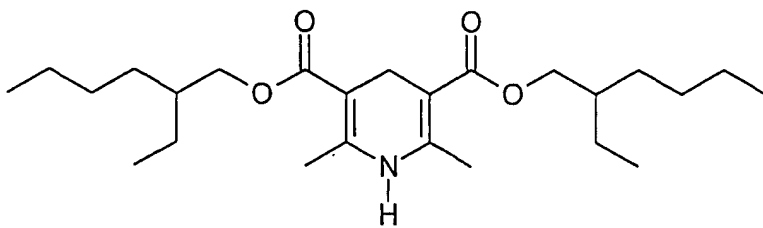
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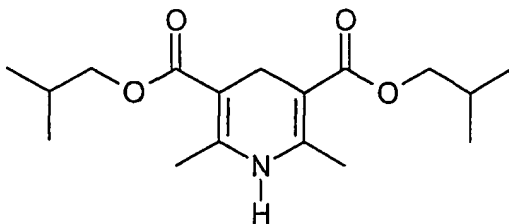
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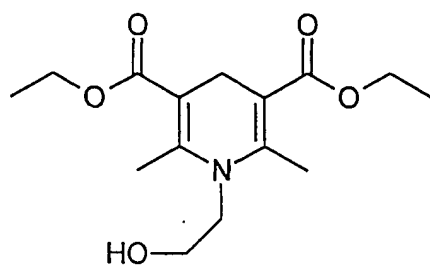


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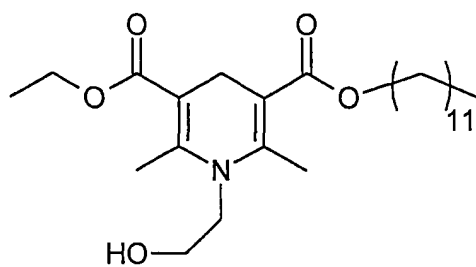


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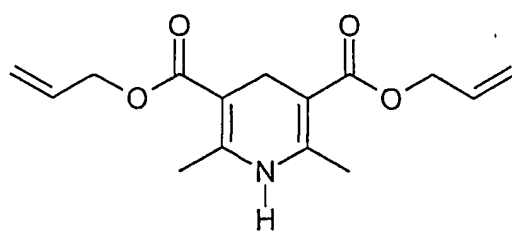
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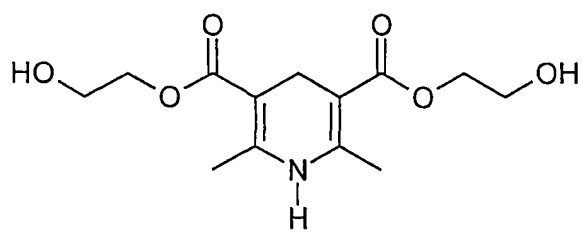
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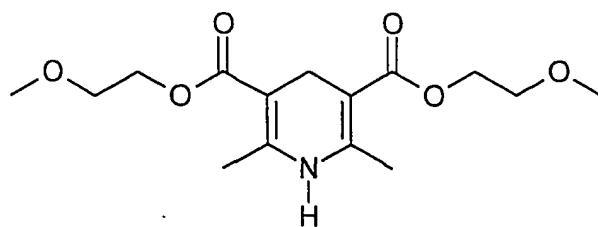
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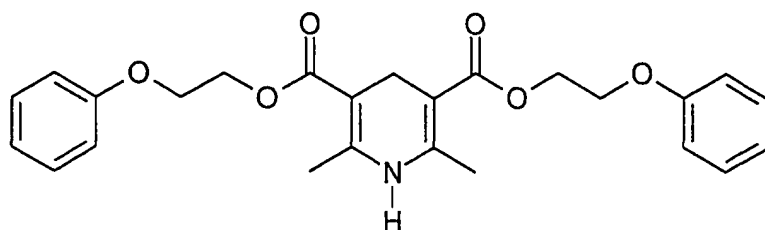


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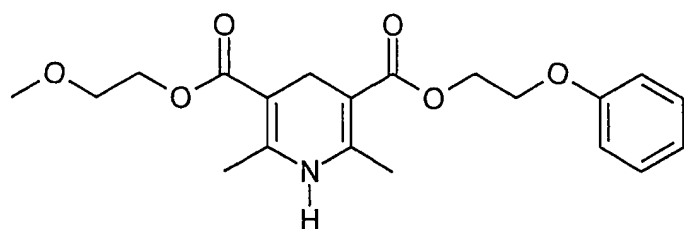


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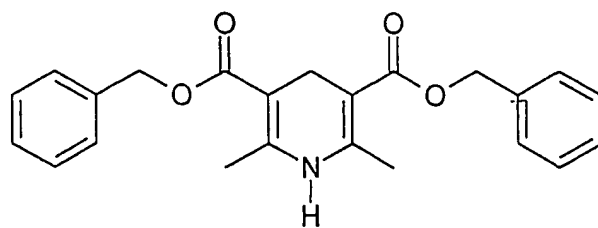
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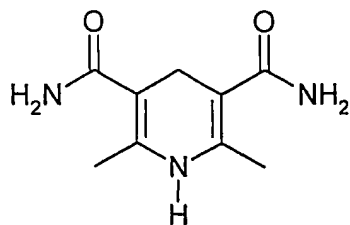
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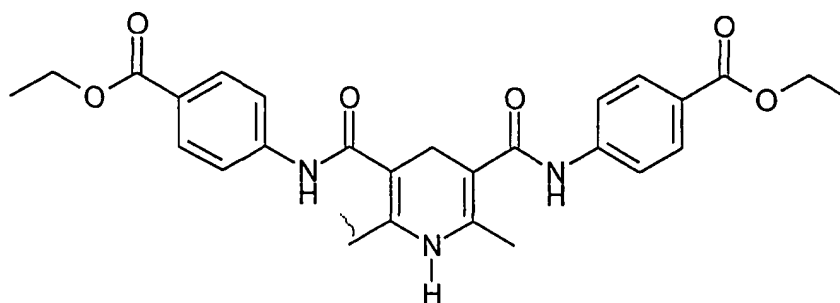
(XX).

- 5 Compound (XX) is particularly preferred, being particularly suitable as it does not bloom from plastic articles prepared from a polymer composition comprising it.

Finally, examples of preferred dihydropyridine diamides are



(XXI), and



(XXII).

The preparation of the monomeric dihydropyridine derivatives contained in the stabilizer composition of the invention is known to the skilled person and is described, e.g., in A. Hantzsch, *Liebigs Annalen der Chemie*, Vol. 215, 1, 72 (1882) and A. M. Van Rhee et al., *Journal of Medicinal Chemistry*, Vol. 39, (15), 2980 - 2989 (1996).

As stated above, the stabilizer composition of the present invention does not comprise any beta-diketone. Not only is the use of such compounds costly and ineffective, they also have to be combined with a metal, such as Zn, to become active, said Zn being less desired. Preferably, the stabilizer composition of the present invention comprises one or more polyols, one or more monomeric dihydropyridine derivatives, one or more acid scavengers, and optionally one or more oxidizing agents. More preferably, the compositions according to the invention do not comprise any further colour stability improving components such as triketones, beta-aminocrotonates, and beta-keto esters. It is further preferred, particularly when the stabilizer is used in rigid PVC grades, that also no further heat stability improving components, such as epoxy compounds, are comprised in the stabilizer compositions of the present invention.

The oxidizing agents that are optionally used in accordance with the present invention are of the conventional type. Suitably one or more oxidizing agents are used that are selected from the group consisting of Li, K, Na, Ca, Mg, Ba, Sr, Zn, Al, La or Ce perborates, perchlorates, persulfates, and/or percarbonates as well as peroxides, including inorganic peroxides like CaO_2 , organic hydroperoxides, and peroxyacids, including perlauric acid and metachloro perbenzoic acid. If a peroxide is chosen, care has to be taken that it is not fully decomposed during the initial processing of the PVC, so that sufficient peroxide is left to be active during the formation of the finished PVC article. Typically, this means that peroxides are to be used with a half life, measured in the conventional way, of 0.1 hour at temperatures above 170°C , preferably above 180°C . Preferably, the strong oxidizing agent is used in such an amount that there is no residual oxidizing agent in the finished article. In view of safety considerations, the oxidizing agents may be used in a "dissolved" form wherein they are (pre)mixed with one or more of the other ingredients of the stabilizer composition. Most preferred is the use of one or more perchlorates, such as potassium and sodium perchlorate. They may be used in the pure, hydrated, or dissolved form, depending on the circumstances. Suitably, the oxidizing agent, or combination of oxidizing agents, is used in an amount of 0-5 %w/w, preferably 0-2 %w/w.

Most preferably, the stabilizer composition of the present invention is free of any heat and colour stability improving components apart from the polyol, monomeric dihydropyridine derivative, acid scavenger, and optional perchlorate. Thus, most preferably, the present invention is directed to a stabilizer composition consisting essentially of 1.5 - 23 %w/w of at least one polyol, 1.5 - 46 %w/w of at least one acid scavenger, such as

hydrotalcite, 3.0 - 31 %w/w of at least one monomeric dihydropyridine derivative selected from the group of substituted or unsubstituted dihydropyridine dicarboxylic acid esters, ester amides, and diamides, optionally 0 - 5 %w/w of one or more oxidizing agents, and 0 - 94 %w/w of one or more additives, based on the total weight of the stabilizer composition, with an "additive" in the sense of the present invention being any compound different from any of the above colour stability improving components. Preferably, the one or more additives neither contain any of the above further colour stability improving components nor contain any of the above further heat stability improving components.

Suitable additives, as presently known in the art, are UV stabilizer, antioxidants, lubricants, plasticizers, reinforcing materials, optical brighteners, fillers, pigments, gelling agents, peroxide scavengers, antistatic agents, flame retardants, foaming agents, and IR absorbers, such as carbon fibrils.

If the colour stability, e.g., during storage, handling or practical use is to be improved, conventional UV stabilizers including HALS stabilizers can be added. Conventional UV stabilizers are 2-hydroxy-4-n-octyloxy-benzophenone, benzotriazols, such as 2-(2'-hydroxy-5'-methylphenyl)-benzotriazol, salicylates, such as 4 tert-butyl salicylate, acrylates, such as α -cyano- β , β '-diphenylacrylic acid isooctyl ester, nickel compounds, e.g., nickel-bis[o-ethyl(3,5-di-tert-butyl-4-hydroxybenzyl)phosphonate], diamides, e.g., 4,4'-dioctyloxy-oxanilide, triazines, such as 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine. Conventional HALS stabilizers are, e.g., bis(2,2,6,6-tetramethyl-4-piperidiny)-sebacate, thiodipropionic acid bis-(2,2,6,6-tetramethyl-4-piperidiny) ester.

Suitable antioxidants are, e.g., pentaerythrityl-tetrakis[β -(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate], diglyceryl-bis[β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], phosphonates, phosphonites, and organic phosphites.

- 5 Suitable pigments are, e.g., titanium dioxide, phthalo pigments, and iron oxide (Fe_2O_3).

Suitable lubricants are, e.g., waxes such as montan wax or polyethylene wax, fatty acid esters and fatty acid amides, such as sorbitol-1,6-bis-(C_{12} - C_{22} fatty acid) esters, fatty alcohols, distearyl phthalate, amide waxes,
10 chloroparaffins, glycerol esters, or metal soaps, such as calcium, zinc or aluminium carboxylates.

Examples of suitable plasticizers are bis(2-ethylhexyl)phthalate, and isosorbide bis(octanoate).

Suitable fillers may be selected from chalk, kaolin, China clay, talc,
15 silicates, glass fibres, glass spheres, wood flour, metal oxides, metal hydroxides, soot or graphite.

As peroxide scavengers may be used esters of thiodipropionic acid, such as lauryl, stearyl, myristyl, or tridecyl esters, mercaptobenzimidazole, and the zinc salt thereof, zinc-butyl-dithiocarbamate, dioctadecyl sulphide,
20 pentaerythritol-tetrakis(beta-dodecylmercapto)-propionate, ethylene glycol bismercaptoacetate, or thiodipropionic acid bis(2,2,6,6-tetramethyl-4-piperidyl) ester.

Suitable antistatic agents are, e.g., glycerol monostearate or sulphonates.

Suitable flame retardants are, e.g., aluminium hydroxide, borates, mixed
25 metal hydroxycarbonates.

Preferably, the stabilizer composition contains less than 30,000 ppm of zinc, still more preferably the stabilizer composition contains less than

30,000 ppm of heavy metals, and most preferably it is essentially free of any heavy metal-containing compounds.

Should any discoloration be observed, it may be considered to omit any
5 calcium hydroxide from the stabilizer composition, if present, in particular when the monomeric dihydropyridine derivative comprises the benzyl ester of dihydropyridine dicarboxylic acid. Another alternative in cases of discoloration may be to introduce or increase the level of oxidizing agent and/or to add (further) UV stabilizers.

10

Preferably, the stabilizer composition of the invention contains 20 - 80 %w/w and even more preferably 30 - 50 %w/w of these further additives, based on the total weight of the stabilizer composition.

15 The invention further pertains to the use of the stabilizer composition of the present invention for the stabilization of polymers, especially halogen-containing polymers, e.g., vinyl resins, such as polyvinyl chloride, and copolymers with vinyl chloride or non-vinyl (co)polymers, polyolefin (co)polymers, and/or blends of different copolymers. Preferably, the
20 polymer is polyvinyl chloride.

The present invention additionally pertains to beta-diketone-free polymer compositions comprising the stabilizer composition of the present invention. Preferably, the stabilizer composition is used in an amount of 1 - 10 %w/w,
25 more preferably 2 - 4 %w/w, based on the total weight of the polymer composition.

- Preferably, the polymer composition comprises 0.1 - 2.0, more preferably 0.2 - 1.0, and most preferably 0.3 - 0.6 parts by weight of the polyol, 0.1 - 3.0, more preferably 0.1 - 2.0, and most preferably 0.1 - 0.8 parts by weight of the acid scavenger, such as hydrotalcite, 0.2 - 1.5, more preferably 0.2 - 1.0, and most preferably 0.3 - 0.5 parts by weight of the monomeric dihydropyridine derivative, and 0 - 1, more preferably 0.001 - 0.5, and most preferably 0.005 - 0.1 part by weight of a perchlorate, per 100 parts by weight of the polymer(s) contained in the polymer composition.
- 10 It is preferred that the polymer composition of the invention contains less than 700 ppm of zinc, more preferably less than 700 ppm of any heavy metals, and most preferably is (essentially) free of heavy metals. It is further preferred that the polymer composition does not comprise any colour stability improving components other than the monomeric dihydropyridine derivative, the acid scavenger, the polyol, and optional perchlorate. It is further preferred that the polymer composition does not comprise any heat stability improving components apart from the monomeric dihydropyridine derivative, the acid scavenger, and the polyol. Even more preferably, the polymer composition does not comprise any heat and colour stability improving components apart from the monomeric dihydropyridine derivative, the acid scavenger, and the polyol.
- 15
20

It is noted that the monomeric dihydropyridine derivatives contained in the stabilizer composition of the present invention are generally oxidized to a minor extent to the corresponding pyridine derivative during or after incorporation into the polymer composition. Therefore, the polymer composition of the present invention will generally contain a small amount of the corresponding pyridine derivative. It is further noted that if the

25

stabilizer composition comprises, e.g., sorbitol, the sorbitol may be reduced in part to sorbitan and/or isosorbide, and the polymer composition may contain small amounts of these reduced components.

5 Furthermore, the present invention is directed to a process for preparing the polymer composition of the invention comprising mixing the polymer(s) with the stabilizer composition. This is a conventional process which can be carried out using, e.g. calenders, mixers, compounders, extruders, and the like.

10

The present invention also pertains to the use of the polymer composition of the present invention for the production of moulded articles, such as extrudates and mouldings, e.g., films, fittings, hollow bodies, such as bottles, profiles, sheets, pipes, cables, and household articles. The polymer
15 composition can be brought to the desired shape by means of conventional processes such as extrusion, injection moulding, calendering, coating, and slush moulding. If the article is prepared by extrusion, the dibenzyl ester of the dihydropyridine derivative is particularly preferred as part of the stabilizer composition, as in this case plate out during extrusion can be
20 successfully prevented.

Finally, the present invention is directed to any of the above moulded articles such as films, fittings, hollow bodies, such as bottles, profiles, sheets, pipes, cables, and household articles comprising the polymer
25 composition of the invention.

The invention will be further illustrated by the following examples.

General procedure

A composition as given in Table I below was mixed and subsequently homogenized during gelation on a rolling mill for 5 minutes at 190°C. After the milling time, the samples were removed as sheets.

- 5 The colour stability of the samples was then characterized by determining the CIE values L, a, and b, and the yellowness index YI. The CIE values were determined on press plates in accordance with DIN-5033 and DIN-6174, using a Minolta Chromameter with a DP 301 data processor. The rating is done according to the CIE-L-a-b system (CIE: Commission
10 International d'Eclairage).

The Yellowness index (YI) was determined on press plates in accordance with ASTM 1925-70.

- The thermal stability was characterized by means of the static heat stability. For the determination of the static heat stability, test pieces of 15 mm x 250
15 mm were cut from the prepared sheets and placed in a Mathis Thermotester Type LTE-T at 200°C. The static heat stability was measured as the time in minutes until complete blackening of the test pieces occurred.

Table I: General sample composition:

Specification	Amount [parts by weight]
S-PVC (Marvylan® S-6808 ex LVM.)	100
chalk (Omya® 95T ex Omya GmbH)	2
calcium stearate	0.30
β -(3,5-di-tert-butyl-4-hydroxyphenyl)- propionic acid-n-octadecyl ester (Lankomark® LE- 384 ex Akcros)	0.10
synthetic paraffin (ex Castor and Astor)	0.45
polyethylene wax (ex BASF)	0.40
oxidized polyethylene wax (ex Allied Chemicals)	0.05
natural paraffin (ex Schuemann)	0.20
titanium dioxide (Kronos® 2220 ex Kronos Titan)	0.20
heat and colour stability improving components	see Examples

Example 1

A polyvinyl chloride composition was prepared as described above. The
 5 resulting polyvinyl chloride composition contained as heat and colour
 stability improving components 0.8 part by weight of 1,4-dihydropyridine-
 2,6-dimethyl-3,5-diethyl carboxylate, 1.2 parts by weight of a magnesium-
 aluminium hydrotalcite (Alcamizer®-1 ex Kyowa), and 0.4 part by weight of
 sorbitol, based on 100 parts by weight of polyvinyl chloride (PVC). The
 10 stability of this composition is given in the Table II below.

Comparative Example A

A polyvinyl chloride composition was prepared in a way identical to that of
 Example 1, except that the stabilizer composition additionally comprised

0.1 part by weight of a beta-diketone, viz. benzoyl-stearoyl-methane (Rhodiastab® 50 ex Rhone Poulenc). The polyvinyl chloride composition of Comparative Example A thus comprised as heat and colour stability improving components 0.8 part by weight of 1,4-dihydropyridine-2,6-dimethyl-3,5-diethyl carboxylate, 1.2 parts by weight of the magnesium-aluminium hydrotalcite, 0.4 part by weight of sorbitol, and 0.1 part by weight of a beta-diketone, based on 100 parts by weight of polyvinyl chloride. As can be seen from Table II below, the stability of the polyvinyl chloride composition was identical to that of Example 1. In other words, despite the presence of a beta-diketone as additional heat and colour stabilizer, no improvement in heat and colour stability could be achieved. This Example clearly shows that beta-diketone, which is essential in the stabilizer composition of EP-A-0 362 012, can be dispensed with in the stabilizer composition of the present invention.

15

Comparative Example B

A polyvinyl chloride composition was prepared in a way identical to that of Example 1, except that the stabilizer composition comprised a beta-diketone, viz. benzoyl-stearoyl-methane (Rhodiastab® 50 ex Rhone Poulenc) instead of the sorbitol. The polyvinyl chloride composition of Comparative Example B thus comprised as heat and colour stability improving components 0.8 part by weight of 1,4-dihydropyridine-2,6-dimethyl-3,5-diethyl carboxylate, 1.2 parts by weight of the magnesium-aluminium hydrotalcite, 0.4 part by weight of the beta-diketone, based on 100 parts by weight of polyvinyl chloride. This polyvinyl chloride composition thus was prepared as claimed in EP-A-0 362 012. As can be seen from Table II below, the static heat stability and the yellow index are significantly worse than those of Example 1.

Comparative Example C

A polyvinyl chloride composition was prepared in a way identical to that of Example 1, except that the stabilizer composition contained 0.8 part by weight of the polydihydropyridine of the only Example of EP-A-0 716 123 (Synesal® M ex Lagor) instead of the monomeric dihydropyridine derivative of Example 1. The polyvinyl chloride composition of Comparative Example C thus contained as heat and colour stability improving components 0.8 part by weight of the polydihydropyridine, 1.2 parts by weight of the magnesium-aluminium hydrotalcite, and 0.4 part by weight of sorbitol, based on 100 parts by weight of polyvinyl chloride. The stability of this composition is given in Table II below. As can be seen from this Table, the stability is significantly worse than that of Example 1. This experiment proves that the use of the monomeric dihydropyridine derivative of the present invention is clearly advantageous over the use of a polydihydropyridine as disclosed in EP-A-0 716 123.

Comparative Example D

A polyvinyl chloride composition was prepared in a way identical to that of Example 1, except that 0.8 part by weight of a beta-diketone, viz. benzoyl-stearoyl-methane (Rhodiastab® 50 ex Rhone Poulenc) was used instead of the monomeric dihydropyridine derivative. The polyvinyl chloride composition of Comparative Example D thus contained as heat and colour stability improving components 0.8 part by weight of the beta-diketone, 1.2 parts by weight of the magnesium-aluminium hydrotalcite, and 0.4 part by weight of the sorbitol, based on 100 parts by weight of polyvinyl chloride. The stability of this composition is given in Table II below. This Table shows that the stability of the composition of Comparative Example D is significantly worse than that of Example 1. Consequently, if the monomeric

dihydropyridine derivative is replaced by a beta-diketone, the stability of the polymer composition is reduced considerably.

Comparative Example E

- 5 A polyvinyl chloride composition was prepared in a way identical to that of Example 1, except that the stabilizer composition did not contain any hydrotalcite or sorbitol. As heat and colour stability improving component the polyvinyl chloride composition thus exclusively contained 0.8 part by weight of the 1,4-dihydropyridine-2,6-dimethyl-3,5-diethylcarboxylate. The
10 stability of this composition is given in Table II below. As can be seen from this Table, the stability is significantly worse than that of Example 1.

Comparative Example F

- A polyvinyl chloride composition was prepared in a way identical to that of
15 Example 1, except that the stabilizer composition did not contain any dihydropyridine derivative or sorbitol. As heat and colour stability improving component the polyvinyl chloride composition thus exclusively contained 1.2 parts by weight of the magnesium-aluminium hydrotalcite, based on 100 parts by weight of polyvinyl chloride. The stability of this composition is
20 given in Table II below. As can be seen from this Table, the stability is significantly worse than that of Example 1.

Comparative Example G

- A polyvinyl chloride composition was prepared in a way identical to that of
25 Example 1, except that the stabilizer composition did not contain any dihydropyridine derivative or hydrotalcite. As heat and colour stability improving component the polyvinyl chloride composition thus exclusively contained 0.4 part by weight of the sorbitol, based on 100 parts by weight

of polyvinyl chloride. The stability of this composition is given in Table II below. As can be seen from this Table, the stability is significantly worse than that of Example 1.

5 Comparative Example H

A polyvinyl chloride composition was prepared in a way identical to that of Example 1, except that the stabilizer composition did not contain any sorbitol. As heat and colour stability improving components the polyvinyl chloride composition thus exclusively contained 0.8 part by weight of the
10 1,4-dihydropyridine-2,6-dimethyl-3,5-diethyl carboxylate and 1.2 parts by weight of the magnesium-aluminium hydrotalcite, based on 100 parts by weight of polyvinyl chloride. The stability of this composition is given in Table II below. As can be seen from this Table, the stability is significantly worse than that of Example 1.

15

Comparative Example I

A polyvinyl chloride composition was prepared in a way identical to that of Example 1, except that the stabilizer composition did not contain any hydrotalcite. As heat and colour stability improving components the
20 polyvinyl chloride composition thus exclusively contained 0.8 part by weight of the 1,4-dihydropyridine-2,6-dimethyl-3,5-diethylcarboxylate and 0.4 part by weight of the sorbitol, based on 100 parts by weight of polyvinyl chloride. The stability of this composition is given in Table II below. As can be seen from this Table, the static heat stability of the composition is about 8
25 minutes worse than that of the composition of Example 1.

Comparative Example J

A polyvinyl chloride composition was prepared in a way identical to that of Example 1, except that the stabilizer composition did not contain any 1,4-dihydropyridine-2,6-dimethyl-3,5-diethylcarboxylate. As heat and colour stability improving components the polyvinyl chloride composition thus exclusively contained 1.2 parts by weight of the magnesium-aluminium hydrotalcite and 0.4 part by weight of the sorbitol, based on 100 parts by weight of polyvinyl chloride. The stability of this composition is given in Table II below. As can be seen from this Table, the stability is significantly worse than that of Example 1.

The above Comparative Examples E - J clearly show that if one or more of the heat and colour stability improving components of the present invention are absent, the heat and colour stability of the polyvinyl chloride composition is reduced considerably.

Table II: Stability of the polyvinyl chloride compositions of Example 1 and Comparative Examples A - J

Example	Static heat stability [minutes]	YI	L	a	b
1	46.2	33.9	87.8	-4.0	20.6
A	43.6	29.3	87.9	-4.24	18.1
B	40.8	>>33.9	/**	/	/
C	31.4	79.2	79.3	3.95	44.9
D	22.7	96.1	61.5	22.5	32.5
E	27.0	65.4	83.7	0.4	38.4
F	.*	55.4	33.9	15.7	6.9
G	30.0	79.1	44.4	21.6	15.2

H	39.6	40.4	88.2	-6.13	26.0
I	37.8	33.6	85.1	-2.4	19.3
J	20.0	67.0	38.7	18.8	10.2

*turned dark immediately when the test was started

**not measured

Example 2

- 5 A polyvinyl chloride composition was prepared as described in the general procedure. The resulting polyvinyl chloride composition contained as heat and colour stability improving components 0.4 part by weight of 1,4-dihydropyridine-2,6-dimethyl-3,5-dibenzyl carboxylate, 0.3 part by weight of a magnesium-aluminium hydrotalcite (Alcamizer®-1 ex Kyowa), and 0.3
- 10 part by weight of sorbitol, based on 100 parts by weight of polyvinyl chloride. The static heat stability of this composition was 33.0 minutes, the yellow index was 47.8, L was 85.5, a was -5.3, and b was 29.9.

This Example shows the suitability of the dibenzyl ester of the dihydropyridine derivative in the stabilizer composition of the present

15 invention.

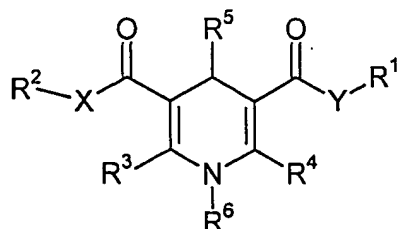
Example 3

- A polyvinyl chloride composition was prepared as described in the general procedure. The resulting polyvinyl chloride composition contained as heat
- 20 and colour stability improving components 0.4 part by weight of 1,4-dihydropyridine-2,6-dimethyl-3,5-dibenzyl carboxylate, 0.3 part by weight of a magnesium-aluminium hydrotalcite (Alcamizer®-1 ex Kyowa), and 0.3 part by weight of inulin, based on 100 parts by weight of polyvinyl chloride. The static heat stability of this composition was 30.1 minutes, the
- 25 yellowness index was 60.1, L was 84.5, a was -3.0, and b was 36.9.

This Example shows the suitability of the dibenzyl ester of the dihydropyridine derivative and of inulin in the stabilizer composition of the present invention.

Claims

1. A stabilizer composition for polymers which composition is essentially free of beta-diketone and comprises 1.5 - 23 %w/w of at least one polyol, 1.5 - 46 %w/w of at least one acid scavenger, 3.0 - 31 %w/w of at least one monomeric dihydropyridine derivative selected from the group consisting of substituted or unsubstituted dihydropyridine dicarboxylic acid esters, ester amides, and diamides, 0 - 5 %w/w of one or more oxidizing agents, preferably perchlorates, and 0 - 94 %w/w of one or more additives, all weight percentages being based on the total weight of the stabilizer composition.
2. The stabilizer composition of claim 1 wherein the composition consists essentially of 1.5 - 23 %w/w of at least one polyol, 1.5 - 46 %w/w of at least one acid scavenger, 3.0 - 31 %w/w of at least one monomeric dihydropyridine derivative, 0 - 5 %w/w of one or more oxidizing agents, and 0 - 94 %w/w of one or more additives which are different from any colour stability improving components, all weight percentages being based on the total weight of the stabilizer composition.
3. The stabilizer composition of claim 1 or 2 wherein the monomeric dihydropyridine derivative satisfies the formula



wherein X and Y are independently chosen from O or NR with R being selected from the group of substituted or unsubstituted alkyl, alkenyl, cycloalkyl, aryl, alkaryl or arylalkyl groups having up to 20 carbon atoms, or hydrogen, R¹ and R² are independently selected from the group of substituted or unsubstituted alkyl, alkenyl, cycloalkyl, aryl, alkaryl or arylalkyl groups having up to 20 carbon atoms, or hydrogen in the case of X and/or Y being NR, and R³, R⁴, R⁵, and R⁶ are independently selected from hydrogen or substituted or unsubstituted alkyl, alkenyl, cycloalkyl, aryl, alkaryl or arylalkyl groups having up to 22 carbon atoms.

4. The stabilizer composition of any one of the preceding claims wherein the polyol comprises sorbitol and the acid scavenger comprises a hydrotalcite.
5. The stabilizer composition of any one of the preceding claims wherein the additives are selected from the group of UV stabilizers, antioxidants, lubricants, plasticizers, reinforcing materials, optical brighteners, fillers, pigments, gelling agents, peroxide scavengers, antistatic agents, flame retardants, foaming agents, and IR absorbers.
6. The stabilizer composition of any one of the preceding claims wherein the stabilizer composition is essentially free of heavy metals.
7. Use of the stabilizer composition of claims 1 - 6 for the stabilization of polymers.

8. The use of claim 7 wherein the polymer comprises at least one halogen-containing polymer.
9. The use of claim 8 wherein the polymer is polyvinyl chloride.
- 5 10. A polymer composition comprising at least one polymer and the stabilizer composition of claims 1 - 6 wherein the polymer composition is essentially free of beta-diketone.
- 10 11. The polymer composition of claim 10 wherein the polymer composition comprises 0.1 - 2.0 parts by weight of at least one polyol, 0.1 - 3.0 parts by weight of at least one acid scavenger, 0.2 - 1.5 parts by weight of at least one monomeric dihydropyridine derivative, and 0 - 1 parts by weight perchlorate, per 100 parts by weight of the polymer(s) contained
- 15 in the polymer composition.
12. The polymer composition of claim 10 or 11 wherein the polymer comprises a chlorine-containing polymer.
- 20 13. The polymer composition of claim 12 wherein the polymer is polyvinyl chloride.
14. The polymer composition of claims 10 - 13 wherein the polymer composition is free of heavy metals.
- 25 15. Use of the polymer composition of claims 10 - 14 for the production of moulded articles.

16. A moulded article comprising the polymer composition of claims 10 - 14.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 01/07560

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08K13/02 C08L27/06 //(C08K13/02,5:053,5:3432,3:22)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 419 794 A (HUELS CHEMISCHE WERKE AG) 3 April 1991 (1991-04-03) page 6, line 15 -page 7, line 5; tables	1-16
X	EP 0 524 354 A (WITCO CORP) 27 January 1993 (1993-01-27) claims; examples	1-16
A	EP 0 716 123 A (CIBA GEIGY AG) 12 June 1996 (1996-06-12) cited in the application examples	1-16

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

Z document member of the same patent family

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0419794	A	03-04-1991	DE 3932048 A1	04-04-1991
			CA 2026034 A1	27-03-1991
			DD 298124 A5	06-02-1992
			EP 0419794 A1	03-04-1991
			JP 3122151 A	24-05-1991
			US 5049602 A	17-09-1991
EP 0524354	A	27-01-1993	CA 2047361 A1	23-01-1993
			US 5102933 A	07-04-1992
			EP 0524354 A1	27-01-1993
EP 0716123	A	12-06-1996	US 5814691 A	29-09-1998
			AT 178629 T	15-04-1999
			AU 696696 B2	17-09-1998
			AU 4026795 A	20-06-1996
			BR 9505722 A	23-12-1997
			CA 2164677 A1	10-06-1996
			DE 59505583 D1	12-05-1999
			DK 716123 T3	18-10-1999
			EP 0716123 A2	12-06-1996
			ES 2132582 T3	16-08-1999
			JP 8245849 A	24-09-1996
			TW 424105 B	01-03-2001
			US 6136900 A	24-10-2000
			ZA 9510434 A	18-06-1996